Synthesis, Characterization and Structure of Dioxomolybdenum(VI) Complexes of Aroylhydrazones

A Dissertation

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CERTIFICATE

This is to certify that the dissertation entitled "*Synthesis, Characterization and Structure of Dioxomolybdenum(VI) Complexes of Aroylhydrazones*" submitted by Swastika Mitra of the Department of Chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtain in the bona fide project work carried out by her under my guidance and supervision. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

I further certify that to the best of my knowledge she bears a good moral character.

Date: 03/05/2012

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1. INTRODUCTION

The coordination chemistry of metal complexes with Schiff base ligands has attracted continous attention for the synthetic chemist due to their ease of synthesis, stability under a variety of oxidative and reductive conditions. The ability of molybdenum to form stable complexes with oxygen-, nitrogen- and sulfur-containing ligands led to the development of molybdenum Schiff base complexes which are efficient catalysts [1-8]. Schiff base ligands are effective in constructing supramolecular architectures [9-10]. Synthesis of homo- and heteromettalic complexes having Schiff base ligands which can accommodate different metal centres involving various coordination modes with varied stereochemistry were studied [11]. This feature is applied for modelling active sites in biological systems [12]. The activity of these complexes varies markedly with the type of ligands and coordination sites [13-17] and also have biological activities such as antibacterial, antiviral, antifungal activities and anticancer drugs [18-28].

My investigations has demonstrated that the transition metal complexes (Ru(II), Pd(II), Pt(II) and Hg(II)) with Schiff bases of 1-hydroxy-2-acetonaphthone containing chalcogen functionalities have wide range of applications in C–C coupling reactions. The Pd (II) complexes with these Schiff base have been found promising as homogeneous catalyst for Heck and Suzuki reactions. These types of molecules were also studied as proton transfer prototype in gas, solution and nanocavities [29].

Mo (VI) complexes of some selected acid hydrazides with ONO donor ligands may mimic the active sites of some oxotransfer molybdoenzyme [30, 31] and hence it is of great interest in bio inorganic chemistry. The coordination compounds of aroylhydrazones have been reported to act as enzyme inhibitors [32-34] and are useful due to their pharmacological applications [35]. The 3-hydroxy-2-naphthohydrazone based vanadium complexes showed the most powerful catalytic

activity in oxidation of various terminals, cyclic and phenyl substituted olefins [36]. To the best of my knowledge, there were no report of Mo complexes of Schiff bases of HAN having hydrazide ligand and also Schiff base by condensation of 2-naphthohydrazide with different aldehydes.

I have been studying the chemistry of dioxomolybdenum(VI) complexes using O-N donor hydrazide ligands and to explore its chemistry towards the substrate binding and oxotransfer properties as it has one or two "open" coordination sites and these species have frequently been considered as models of enzymatic reaction and catalytic sites. In this dissertation, I have reported synthesis and characterisation of two different hydrazide with aromatic aldehydes and also characterized their corresponding dioxomolybdenum complexes. All the synthesized ligands and their corresponding Mo (VI) complexes have been characterized by elemental analysis, and several spectroscopic (IR, UV–Vis and NMR) techniques .One (complex-**2**) of the three complexes reported here, has also been structurally characterized by single crystal X-Ray crystallography. The X-ray studies of other two synthesized Mo complexes are under process.

2. Experimental:

2.1. Materials:

Chemicals were procured from renowned company like Aldrich E. Merck, and used without further purification. HPLC grade DMF was used for spectroscopic and electronic spectral studies and ethanol, methanol were used for synthesis of ligands and metal complexes. $MoO_2(acac)_2$ has been synthesized following a published method [24, 30, 31].

2.2. Physical Measurements:

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer. IR spectra were recorded on a Perkin–Elmer Spectrum RXL. Electronic spectra were recorded on a Perkin-Elmer Lamda spectrophotometer. ^1H NMR spectra were recorded with a Bruker Ultrashield 400 MHz spectrometer using $SiMe_4$ as an internal standard.

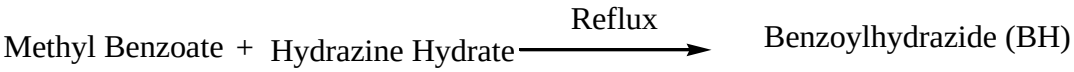
2.3. Synthesis of the Ligands:

The synthesis of our final ligand consists of two steps.

Step-1: Synthesis of acid hydrazide

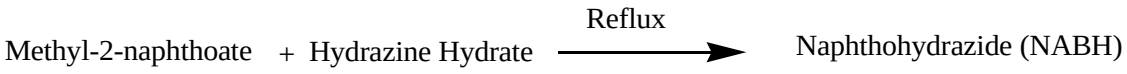
2.3.1. Synthesis of Benzoyl hydrazide (BH):

The acid hydrazide was prepared by known [24] method which is schematically shown below:



Found (calc. for $C_7H_8N_2O$): C 61.56(61.76), H 5.81 (5.88), N 20.32 (20.58). Yield: 74 %

2.3.2. Synthesis of Naphthohydrazide (NABH):

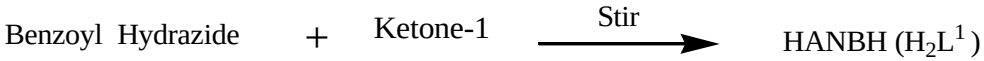


Found (calc. for $C_{11}H_{10}N_2O$): C 70.73 (70.96), H 5.15 (5.37), N 14.90 (15.05). Yield: 65 %

Step-2: Synthesis of Schiff's base ligand

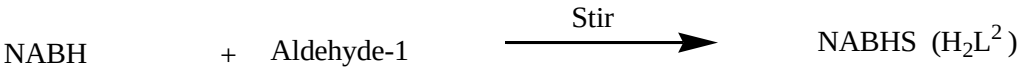
All the three Schiff's base ligands used in this study were prepared following same method by stirring carbonyl compounds and the respective hydrazide in equimolar ratio. A typical synthesis is described below

2.3.3. Synthesis of benzoylhydrazone of 2-Hydroxyacetonaphthone (HANBH):



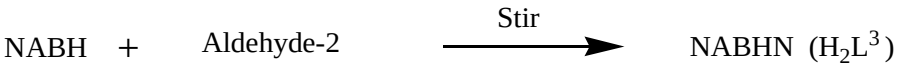
Found (calc. For $C_{19}H_{16}N_2O_2$): C 74.89 (75), H 5.09 (5.26), N 9.10 (9.21). Yield: 68 %

2.3.4. Synthesis of Naphthohydrazone of 2-Hydroxybenzaldehyde (NABHS):



Found (calc. For $C_{18}H_{14}N_2O_2$): C 74.23 (74.48), H 4.67 (4.82), N 9.43 (9.65).

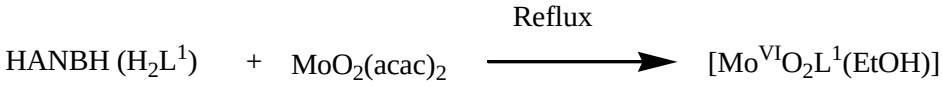
2.3.4. Synthesis of Naphthohydrazone of 2-Hydroxynaphthaldehyde (NABHN):



Found (calc. For $C_{22}H_{16}N_2O_2$): C 77.51 (77.64), H 4.59 (4.70), N 8.10 (8.23).

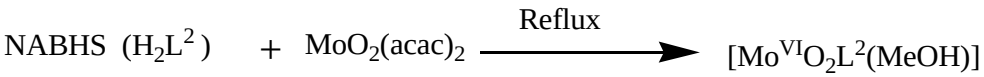
2.4. Synthesis of metal complexes

2.4.1. Complex 1, [MoO_2L^1EtOH)]



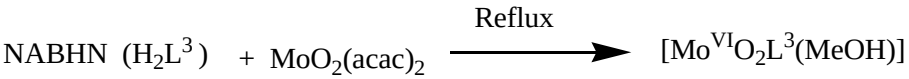
Found (calc. For $C_{21}H_{20}N_2O_4Mo$): C 54.58 (54.78), H 4.29 (4.34), N 6.02 (6.08). Yield: 52 %

2.4.2. Complex 2, [MoO_2L^2(MeOH)]:



Found (calc. For $C_{19}H_{16}N_2O_4Mo$): C 52.55 (52.77), H 3.65 (3.70), N 6.23 (6.48). Yield: 50 %

2.4.3. Complex 3, [MoO_2L^3 (MeOH)]:



Found (calc. For $C_{23}H_{18}N_2O_4Mo$): C 57.10 (57.26), H 3.59 (3.73), N 5.63 (5.80). Yield: 54 %

3. Results and Discussions

3.1 Spectral characteristics:

*IR Spectra of the ligand HANBH [H_2L^1] and Complex **1**[$Mo^{VI}O_2L^1(EtOH)$]:*

The complex do not exhibit the ligand bands at 3336 cm^{-1} [ν(OH)], 3132 cm^{-1} [ν(NH)], and 1652 cm^{-1} [ν(C=O)] [24] . Characteristic strong bands at 1622 cm^{-1} and 1572 cm^{-1} due to ν(C=N) and ν(C=C/aromatic) stretching modes of the ligand [30], but after metallation the characteristic bands are shifted at 1596 cm^{-1} and 1547 cm^{-1} region. The Mo=O stretching modes occur as a pair of sharp strong peaks in the 941-863 cm^{-1} range [24, 30, 31].

NMR spectra of the ligand H_2L^1 and Complex 1[$Mo^{VI}O_2L^1(EtOH)$]:

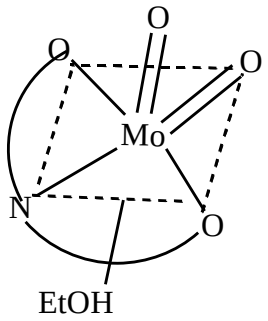
The ^1H NMR spectrum of the free ligand exhibits an OH (phenolic) resonance at δ = 10.31 ppm, NH (imine) resonance at δ = 9.55 ppm and CH_3 resonance at δ = 2.34 ppm. All the aromatic proton signals expected from the ligand and complex are clearly observed in the expected region at δ = 6.91 ppm - 8.08 ppm. The signal for the OH and NH protons disappeared, indicating the deprotonation of the phenolic OH and NH groups in the complex. After metallation the CH_3 proton resonace is appeared at δ = 2.91 ppm.

Electronic Spectra of complex 1 [$Mo^{VI}O_2L^1(EtOH)$]:

The electronic spectrum (In DMSO) of this complex was obtained at 423 nm due to ligand to metal [L–Mo (dπ) LMCT] charge transfer [24, 30, 31]. Two strong absorptions are also located in the 257 – 329 nm range, which are assignable to intraligand transitions.

3.2. Possible Structures of Complex 1

As all the ligands have extensive π-delocalization across their backbone, so they try to remain in planar disposition. Thus they will occupy meridional planes in a distorted octahedral coordination sphere. The proposed structures of the complexes **1** is given below.



$[Mo^{VI}O_2L^1(EtOH)]$

Possible structure of complex 1

4. Conclusion

Three Schiff's base hydrazone ligands were synthesized and characterized by IR spectra and elemental (C, H, N) analysis. The basic and electronic property of these ligands has been nicely explored in the syntheses of various dioxomolybdenum(VI) complexes. One (complex **1**) of the three complexes reported here has been fully characterized by IR, UV-visible, NMR spectroscopy. This study indicates that the hydrazone ligand (e.g., H_2L^1) has the normal tendency to form monomeric complex coordinated in the form of dianionic tridentate manner.

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